CATALYSIS IN DIRECT LIQUEFACTION OF COAL

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INTRODUCTION

In view of the recent National Research Council study (1) and the present National Energy Strategy (2), the Pittsburgh Energy Technology Center (U.S. Department of Energy) is actively pursuing the Direct Liquefaction Program to develop technologies for producing low-cost liquid fuels from coal. A brief overview of the ongoing Direct Liquefaction Program is given below. This program broadly encompasses laboratory and bench-scale developments of promising new concepts, as well as proof-of-concept evaluation in pilot-scale, two-stage liquefaction units. Of the various areas being studied in this program, improved catalysts could play a major role in lowering thermal severity, improving product yields/selectivity, and improving process configuration. Thus, the catalysts used in the ongoing two-stage liquefaction studies and some of the current activities in the catalysis research are outlined in this paper.

OVERVIEW OF THE DIRECT LIQUEFACTION PROGRAM

The overall objective of the Pittsburgh Energy Technology Center's (PETC) Direct Liquefaction Program is to bring the liquefaction technology to commercial readiness in an environmentally acceptable manner, and some of the current activities directed toward this objective are outlined below.

Two-Stage Liquefaction Program

Direct liquefaction process testing is continuing at Hydrocarbon Research Inc. (HRI) and Amoco Oil Company. Future research will focus on the effects of coal cleaning/pretreatment, dispersed catalysts, preconversion processing, solids separation methods, bottoms processing, on-line hydrotreating, and solvent quality improvement.

Advanced Process Concepts Program

One of the main objectives of this program is to conduct fundamental studies and exploratory research to develop improved process configurations in direct liquefaction. The work being performed by some PETC contractors is briefly outlined as follows. The University of Kentucky Research Foundation is focusing on a two-stage low-rank coal liquefaction process that has oil agglomeration, fluid coking, and solvent dewaxing as the main features. Improvements in process operation, coal conversion, and product yields are anticipated. SRI is evaluating novel dispersed catalysts and improved reaction chemistry (e.g., use

of $CO+H_2$) for low-rank coals. This program will focus on reducing regressive reactions and increasing product quality in liquefaction. HRI is studying the merits of integrating two-stage liquefaction with fixed-bed hydrotreating to give improved products. Amoco Oil Company is evaluating the following processing steps to improve process operability during liquefaction of low-rank coals: conventional coal cleaning, coal pretreatment with aqueous SO_2 solutions to remove alkali metals from coal, impregnation of coal with a catalyst, and bottoms processing (e.g., deasphalting, coking). The Canadian Energy Development, Inc. (with Alberta Research Council) is evaluating a two-stage process consisting of oil agglomeration, coal slurry pretreatment, and hydroconversion. In this study, use of a dispersed catalyst and $CO+H_2O$ system in a counter-flow reactor is proposed for process improvement.

Baseline Design and System Analysis

A conceptual baseline design of a two-stage direct coal liquefaction process, sponsored by PETC, is being performed by Bechtel and Amoco. This baseline study includes development of a process simulation model applicable over a certain range of capacities and process options involving coal cleaning, reactor configuration, vacuum bottoms processing, and hydrogen production methods. The model simulates a commercial liquefaction facility to predict yields and economics for different processing schemes. The data obtained at the Wilsonville Advanced Coal Liquefaction Research and Development Facility in Run 257 with Illinois No. 6 coal from Burning Star No. 2 mine and Amocat-1C catalyst in a two-stage catalytic liquefaction process is being utilized as the base case.

Coprocessing Program

Coprocessing, in which coal is processed along with a heavy petroleum residuum, is considered to be a variation of direct liquefaction. Some of the present studies in coprocessing are focusing on understanding possible synergism between coal and petroleum residuum, merits of dispersed catalysts, and recycle effects. Bench-scale studies are being carried out at UOP in a slurry reactor and at HRI in a two-stage ebullated-bed reactor system. These studies are being assessed for their technical and economic merits.

Refining, Upgrading, and End-Use Testing Program

Although the current two-stage liquefaction products are lower in heteroatom contents and higher in hydrogen compared to previous single-stage products, the two-stage products require additional refining/upgrading to meet commercial fuel specifications.   Studies will be performed to produce refinery feeds and specification products in order to assess the technology required for refining and also to test the products for their emission properties.

Generic Bench-Scale Unit

An integrated, continuous-flow bench-scale unit (BSU) will be built at PETC to screen, develop, and improve new process concepts in direct liquefaction. This unit will have a capacity of 200 pounds of coal feed per day. This BSU will have the flexibility to operate over a wide range of conditions with different ranks of coals and different reactor types (i.e., slurry, ebullated-bed, fixed-bed). It is anticipated that this unit will be ready for operation by 1993. During the design and construction of this generic BSU, promising new approaches being developed by PETC contractors will be evaluated for testing in this unit.

TWO-STAGE LIQUEFACTION CATALYSTS

Catalysis plays a major role in determining coal and resid conversions and distillate selectivity in direct liquefaction. Although the inherent mineral matter in coal itself has some catalytic activity, external catalysts must be provided to obtain satisfactory reaction rates and specification products. A description of the status of liquefaction catalysis and catalysts was given in some recent reviews (3, 4). In the catalytic two-stage liquefaction process that was studied at Wilsonville and HRI in the recent past, alumina-supported transition metal catalysts were used in the ebullated-bed reactors to facilitate coal liquefaction and solvent hydrogenation. A brief description of the two-stage liquefaction process is given below to better understand the role and importance of catalysts in each reactor.

Process Description

In the close-coupled two-stage liquefaction, two ebullated-bed reactors are in series followed by a solids separation system. The pulverized feed coal is mixed with coal-derived recyle solvent and hydrogen and preheated before entering the first stage. The slurry in the first stage is continuously recirculated by the use of a pump while the catalyst extrudates are ebullated in an upflow stream. Typical reactor inlet hydrogen partial pressures and reactor average temperatures would be in the ranges of 2300 to 2500 psig and 750 to 810°F, respectively. About 90 wt% of a bituminous coal conversion generally occurs in the first stage, and the degree of hydrogenation and distillate production depend on the operating conditions such as temperature, pressure, catalyst type/charge/age, and space velocity. Depending on the liquefaction conditions, the catalyst could deactivate due to factors such as coking, deposition of minerals and basic compounds, pore mouth plugging, and sintering. To sustain steady catalytic activity in the reactor, some deactivated catalyst must be withdrawn and replaced with fresh catalyst. Because high catalyst deactivation rates require high catalyst replacement rates, developing catalysts that are resistant to rapid deactivation is desirable. Maintaining good catalyst activity in the first stage could facilitate obtaining higher coal conversions, higher solvent quality, and higher resid cracking/hydrogenation.

The first-stage products, which are gases, distillate, resid (resid is typically non-distillable at 850°F and 1 atm), unconverted coal, and ash, may be passed through an interstage separator for removing heteroatom gases (i.e., gases containing sulfur, nitrogen, and oxygen), light hydrocarbon gases, and some distillate before entering the second stage. Separating the heteroatom gases could allow maintaining higher hydrogen partial pressures in the second stage. In addition, undesirable reactions such as methanation could be minimized, especially in low-rank coal operations. The second stage is usually operated under conditions that are favorable for heteroatom removal and further upgrading of coal liquids. Depending on the operating mode, i.e., high/low or low/high, the second stage conditions could be, to some extent, in the range given above for the first stage. The second-stage products are sent to various vapor-liquid and liquid-solid separation systems for product recovery and recycle solvent preparation (5-9).

Supported Catalysts

Generally, in two-stage liquefaction, supported catalysts were used in both

stages for bituminous coals (7-9). On the other hand, a supported catalyst was used in only one stage at Wilsonville in most of the low-rank coal liquefaction studies; some tests with subbituminous coals were, however, made both at HRI and Wilsonville using supported catalysts in both stages.

At Wilsonville, Criterion 324 (Shell 324) unimodal Ni-Mo catalyst was frequently used in recent runs. In addition, Ni-Mo bimodal catalysts were also tested in some runs, e.g., Shell 317 in Run 254, Amocat-1C in Run 257, and EXP-AO-60 in Run 261 (8, 9). These catalysts typically contain 10 to 13 wt% molybdenum and 2 to 3 wt% nickel on alumina. The pore volumes in unimodal and bimodal catalysts are typically in the ranges of 0.4 to 0.5 and 0.7 to 0.8 cc/g, respectively (9). The diameters of small pores in both types of catalysts are usually in hundreds of angstroms (e.g., 100-200 °A); however, the bimodal catalysts are distinguished by the presence of additional pores having diameters in thousands of angstroms (e.g., 1000-2000 °A). The larger pores in bimodal catalysts could facilitate diffusion of large asphaltene molecules and reduce pore mouth plugging.

Satisfactory performance of Criterion 324 was observed, when it was used as the second-stage catalyst in thermal/catalytic mode, in Wilsonville subbituminous coal runs 258 and 260 (8, 10). In these runs, the catalyst replacement rate was in the range of 1.5 to 3 lb/ton coal. Significantly improved performance of the catalytic stage was observed when Criterion 324 was used in the first stage in catalytic/thermal mode in Run 260 (8). It may be pointed out that in these runs, an iron precursor was introduced with coal-solvent slurry to catalyze coal conversion.

High distillate yields and good product qualities were obtained with a deep-cleaned Pittsburgh seam coal, in Wilsonville Run 259, using Criterion 324 catalyst in both stages at a total catalyst replacement rate of 8 lb/ton coal (9). In Run 261, tests were performed with Illinois No. 6 coal using EXP-AO-60 and Criterion 324 catalysts (8). The total catalyst replacement rates in this run were in the range of 3 to 6 lb/ton coal. In Runs 259 and 261, increasing slurry viscosities limited the extent of batch deactivation with Criterion 324 catalyst. Satisfactory process performance was obtained using EXP-AO-60 catalyst at a total catalyst replacement rate of 3 lb/ton coal (8). The physical strength of the bimodal catalysts was of some concern in ebullated-bed reactor operation. For example, when 1/12-inch Amocat-1C cylindrical extrudates were used in Wilsonville Run 257, a significant amount of the initially charged catalyst was found to be broken at the end of the tests (11). However, it appeared that some other bimodal catalysts, i.e., 1/16-inch EXP-AO-60 cylindrical pellets tested in Run 261 and 1/20-inch Shell 317 trilobe pellets tested in Run 254, did not exhibit significant breakage (8, 12).

HRI developed a catalytic two-stage liquefaction process operating in low/high temperature mode using nickel-molybdenum supported catalysts (7). Some of the catalysts tested were 1/32-inch Davison Amocat-1C catalyst, 1/20-inch UOP spherical catalyst, and 1/32-inch Shell 317 cylindrical catalyst. An Illinois No. 6 coal and an Ohio No. 5/6 coal (both bituminous) and a Wyodak subbituminous coal were tested in this process development. In this low/high process, the first-stage catalytic ebullated-bed reactor was operated at low temperatures (about 750°F). At these mild temperatures, coal is thought to dissolve slowly in the recycle solvent allowing the rate of catalytic hydrogenation reactions that regenerate the solvent to be somewhat similar to the rate of coal conversion. Further conversion and upgrading of first-stage products occur in

the second stage operated at higher temperatures. Higher distillate yields and extinction recycle conversion of heavy oils (750°F+ vacuum gas oil) were said to be some of the major achievements in this low/high mode (7).

Some of the recent supported catalyst work at HRI was focused on on-line hydrotreating. On-line hydrotreating with Shell 424, NiMo catalyst, was effective in reducing the heteroatom content in the distillate product. For example, when a distillate having an end-point of about 550°F was hydrotreated, the nitrogen and sulfur contents were reduced from 1280 to 9 ppm and 230 to 14 ppm, respectively. In additional tests, the hydrotreating efficiency was found to be dependent on the feed end-point (13).

Dispersed Catalysts

At Wilsonville, a readily available iron oxide (minus 325 mesh powder) in combination with a sulfiding agent was used routinely in the liquefaction of subbituminous coals. Although this gave satisfactory operation with two-stage coal conversions in the range of 90 to 95 wt%, the iron dispersion might not have been optimum under the liquefaction conditions. In the recent past, a molybdenum precursor was used at Wilsonville in the liquefaction of the Black Thunder mine subbituminous coal (8, 14). The precursor was a complex organic compound (commercial name is Molyvan L) containing molybdenum, sulfur, phosphorous, carbon, and hydrogen. It was used primarily to test the effectiveness of dispersed molybdenum in limiting the solids buildup frequently observed at Wilsonville during the liquefaction of subbituminous coals. Based on preliminary results, it appeared that the solids buildup was mitigated to some extent when the dispersed molybdenum was used (14). Again, as was the case with the iron oxide, it was not certain that the selected molybdenum precursor, Molyvan L, gave optimum active metal dispersion.

HRI recently tested some iron precursors in combination with a supported catalyst. These iron compounds were magnetite (an oxide magnetic pigment) and a pyrrhotite. It was concluded that these compounds had limited catalytic effect (15).

The effectiveness of supported catalysts in obtaining high distillate yields (up to 75-78 wt% maf coal) and good product qualities was demonstrated both at Wilsonville and HRI; however, the application of dispersed catalysts in pilot-scale two-stage liquefaction is yet to be thoroughly examined. Some of the current activities in dispersed catalyst development are outlined below.

CATALYST DEVELOPMENT

As stated earlier, due to high deactivation rates of supported catalysts currently used in pilot-scale process development, aged catalysts must be continually replaced to sustain good catalytic activity. High catalyst replacement rates could contribute significantly to the operating costs in a commercial process. Although regeneration of these catalysts could reduce costs, effective procedures for catalyst regeneration are yet to be demonstrated in pilot-scale operations. In addition, recovery of the metals from spent catalysts is a significant process expense. Hence, PETC is sponsoring research on the development of new and improved catalysts and catalytic processes. Some of these activities are briefly described below.

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Finely Dispersed Iron and Molybdenum Catalysts: In-House Research at PETC

Researchers at PETC are developing advanced procedures to obtain finely divided
forms of iron and molybdenum to yield highly active catalysts for direct coal
liquefaction applications.   Demonstrating the effectiveness of dispersed
catalysts in pilot-scale liquefaction units could allow using slurry reactors in
place of ebullated-bed reactors at lower capital and operating costs.

Commercially available, low-cost iron compounds could be used as precursors for
disposable liquefaction catalysts. However, the activity of catalysts derived
from readily available iron oxides and iron sulfides could be low due to poor
initial dispersion, low surface area, and the tendency to aggregate. PETC is
focusing on preparing ultrafine particles that have significantly larger surface
area and higher activity compared to the conventional catalysts.

The well-dispersed iron catalysts can exhibit superior characteristics for use
in a coal dissolution reactor. In one preparation method, an initial incipient
wetness impregnation of the feed coal with ferric nitrate was carried out.
Subsequently, the high dispersion and interaction with the coal surfaces was
maintained by conversion of the added iron to an insoluble hydrated iron oxide.
Then, activation of this dispersed hydrated iron oxide at about 525°F was shown
to result in an effective disposable catalyst for coal conversion (16, 17).

Under proper activation conditions, two sulfided molybdenum compounds -- ammonium
tetrathiomolybdate and molybdenum trisulfide -- are very good candidates as
precursors for a slurry catalyst. In contrast to alternative non-sulfided
molybdenum catalyst precursors, use of these precursors could reduce the
activation steps and external sulfur requirements while resulting in a highly
active molybdenum disulfide catalyst. Preliminary studies at PETC indicated that
both precursors thermally decompose to a high surface area molybdenum disulfide
if the thermal transition was rapid. The catalytic activity was sufficient to
sustain high coal conversions at molybdenum concentrations as low as 200 to 300
parts per million (18).

Laboratory liquefaction tests were made at PETC to evaluate the aforementioned
iron and molybdenum catalysts. Using iron concentrations as low as 2500 ppm
(based on coal), liquefaction tests were conducted with Illinois No. 6 coal
slurried with coal-derived solvents. Conversions of the coal to distillate and
soluble products at 425°C in H_2+3% H_2S atmosphere for 1 hr compared favorably with
conversions obtained under the same conditions using 1500 ppm of molybdenum (16).
HRI is also currently testing these dispersed iron catalysts prepared at PETC.
Further development of these catalysts is in progress.

Hydrous Metal Oxide Catalysts

Researchers at Sandia National Laboratories are developing catalysts based on
hydrous titanium oxide (HTO) ion exchangers for application in direct
liquefaction. The hydrous metal oxide ion-exchangers are amorphous inorganic
compounds of metals such as Ti, Zr, Nb, and Ta.   They offer significant
advantages as supports in the preparation of catalysts. The following are some
properties of these ion-exchange compounds that make them desirable as supports
for active metals: several active metals or mixtures of metals can be atomically
dispersed over a wide range of concentrations; the ion exchange capacity of the
materials is large, permitting high loadings of active metals; solution chemistry

can be used to provide control of the oxidation state of the active metal; and, these materials have high surface areas. For example, hydrous titanium oxide catalysts were prepared by a technique that consisted of the synthesis of sodium hydrous titanate ion exchange material followed by exchanging the sodium for active metal ions (19).

Preliminary tests indicated that the HTO catalysts, even at low active metal loadings of 1 wt%, were as effective in converting coal to low molecular weight products as a commercial Ni-Mo/Al$_2$O catalyst containing 15 wt% active metals. In addition, for the same oil yield, the HTO catalysts used less hydrogen than the commercial catalyst (19). In recent tests at Amoco, a NiMo HTO catalyst gave similar performance compared to a commercial catalyst, but at only half of the active metal loading (20). This result suggested good dispersion of Ni and Mo on the HTO catalyst.

Metal Carbide and Nitride Catalysts

Researchers at Clarkson University are developing carbides and nitrides of transition metals to be used as catalysts specifically for nitrogen removal from coal liquids. The metal carbides and nitrides are hard, refractory materials that are resistant to corrosion. In a typical procedure, Mo$_2$C was prepared from MoO$_3$ using a CH$_4$/H$_2$ reactant gas. Initially, the precursor MoO$_3$ was reduced to MoO$_2$ producing water. In the next step, further reduction and carburization occured giving Mo$_2$C having a surface area of about 50-90 m^2/g while forming additional water. When ammonia was used in place of CH$_4$/H$_2$, Mo$_2$N having a surface area as high as 225 m^2/g was produced (21).

Amoco recently compared the performances of a bulk molybdenum nitride and an alumina-supported molybdenum carbide with Amocat-1B (Mo/Al$_2$O,) and Shell 324 (NiMo/Al$_2$O,). These tests were conducted in packed-bed reactors (14/20 mesh catalyst size) under the following conditions: 760°F, 2000 psig total pressure, 10000 SCFB hydrogen flow rate. The feed material was a mixture of a coal-derived resid and Panasol (a refinery by-product). Coal-derived distillates were also used in some tests. This preliminary study seemed to indicate that the molybdenum carbide and nitride catalysts gave products that were better than those obtained using Shell 324 and Amocat-1B (20). Moreover, these carbide and nitride catalysts seemed to have higher activity on a per-site basis (turnover rate) compared to the commercial catalysts (21).

SUMMARY

PETC is actively pursuing an advanced, novel concepts research program in direct liquefaction to bring the technology to commercial readiness in the near future. Of the various areas being studied in this program, improved catalysts could play a major role in lowering thermal severity, improving product yields and selectivity, and improving process configuration. The catalysts used in the recent two-stage liquefaction studies at Wilsonville and HRI, and the current activities in catalysis research have been briefly reviewed. The commercial supported catalysts were found to be effective in two-stage liquefaction. Because of high deactivation rates and the need for using ebullated-bed reactors, PETC is also focusing on developing dispersed catalysts which will lead to the use of less capital intensive slurry reactors. Preliminary work at PETC was successful in obtaining finely dispersed, highly active iron and molybdenum catalysts. The PETC Project Office will continue to focus on the development of advanced liquefaction reactor systems to improve the overall economics.

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